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Note

Polyphosphoric acid and anhydrous aluminium chloride catalysed novel rearrangements of 1,5-diaroylcarbohydrazides

A V Karnik* & Rajesh G Kamath
Department of Chemistry, University of Bombay, Vidyanagari, Santacruz (East). Mumbai 400 098

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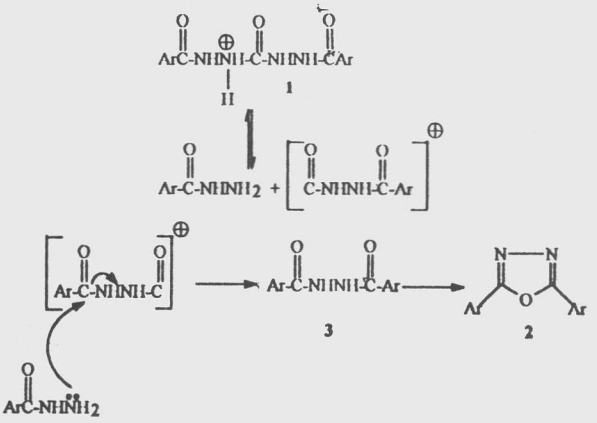
1,5-Diaroylcarbohydrazides **1** on reaction with polyphosphoric acid (PPA) at 150°C for 15 min undergo an interesting rearrangement to afford 2,5-diaryl-1,3,4-oxadiazoles **2**. However, the reaction of **1** with anhydrous aluminium chloride yields 1,2-diaroylhydrazines **3**.

Polyphosphoric acid (PPA) is a versatile reagent in organic chemistry giving rise to a plethora of reactions[1]. Some hydrazino derivatives such as 1-benzyl-2-benzoylhydrazine[2] and benzoylacetone hydrazone[3] were reported to undergo a PPA catalysed rearrangement to afford 2,5-diphenyl-1,3,4-oxadiazole **2** (Ar = Ph). These reports indicated that hydrazino derivatives bearing a good leaving group were suitable for this type of reaction. In view of these reports we considered it worthwhile to find out the effect of PPA on 1,5-diaroylcarbohydrazides **1** containing two hydrazino moieties.

When the reaction of 1,5-diaroylcarbohydrazides **1** was carried out in PPA at 150°C for just 15 min, 2,5-diaryl-1,3,4-oxadizoles **2** were obtained in moderate yields. The formation of **2** could be explained on the basis of rearrangement of **1** to afford the intermediate 1,2-diaroylhydrazine **3** as depicted in Scheme I. The intermediate **3** then looses a molecule of water under the strong dehydrating influence of PPA to give **2**.

To support our hypothesis of intermediate formation of 1,2- diaroylhydrazine **3**, the reaction of 1,5-diaroylarohydrazides **1** was carried out in the presence of anhydrous aluminium chloride which is a good Lewis acid catalyst without a strong dehydrating influence. When 1,5-diaroylcarbohydrazides **1** were heated with anhydrous aluminium chloride at



Scheme I

170-80° for 3 hr, 1,2- diaroylhydrazines **3** were obtained in moderate to good yields.

Experimental

Melting points reported are uncorrected. IR Spectra (cm^{-1}) were recorded on Shimadzu FTIR-4200, and ^{1}HNMR spectra on Varian EM- 360L (60 MHz) spectrometer in $CDCl_3$ (chemical shifts in δ, ppm) using TMS as an internal standard.

Reaction of 1,5-dibenzoylcarbohydrazide (1a, Ar= Ph) in the presence of PPA. Compound **1a** (2g) was dissolved in PPA (prepared from 12 g P_2O_5 and 8mL of H_3PO_4) and the mixture heated on an oil-bath at 150°C for 15 min. The reaction mixture was then cooled to room temperature and was decomposed over crushed ice. It was basified with sodium bicarbonate. The solid obtained was filtered and subjected to SiO_2 column chromatography using $CHCl_3$-EtOAc (90:10) as eluant 2,5-Diphenyl-1,3,4-oxadiazole **2a**, Ar = Ph was obtained in 21.5% yield.

Similarly 1,5-diaroylcarbohydrazides **(1b-e**, Ar = *m*-tolyl, *p*-chlorophenyl and 2-furyl) on heating at 150°C in the presence of PPA gave 1,5- diaryl-1,3,4-oxadiazoles **2b-e.** The characterization data of **2a-e** are given in Table I.

Reaction of 1,5-dibenzoylcarbohydrazide (1a, Ar = Ph) in the presence of anhydrous aluminium chloride. Compounds **1a** (2g) was mixed intimately with finely powdered anhydrous aluminium chloride (5g) and the mixture was heated on an oil-bath for 3 hr at 170-80°C. It was cooled to room teperature and

Table I-Characterization data of 2,5-diaryl-1,3,4-oxadiazoles **2a- e**

Compd*†	Ar	m.p. °C	Yield (%)	Mol. formula	^{1}HNMR(δ, ppm)
2a	Phenyl	137	21.5	$C_{14}H_{10}N_2O$	7-8.3 (m, ArH)
2b	3-Tolyl	80	27.45	$C_{16}H_{14}N_2O$	2.6-3(s, 6H, Ar-CH_3) 7.4- 8.4(m, 8H, ArH)
2c	4-Tolyl	174	27.45	$C_{16}H_{14}N_2O$	2.5 (s, 6H, Ar-CH_3) 7.2- 8.2 (m, 8H, ArH)
2d	4-chlorophenyl	248	45.40	$C_{14}H_8N_2OCl_2$	7.5-8.3 (m,,ArH)
2e	2-Furyl	140-41	35.02	$C_{10}H_6N_2O_3$	6.7-7.8 (m, ArH)

* All the compounds gave satisfactory elemental analyses.
† The co-IRs of the compounds matched with the ones prepared by the literature methods[4].

Table II- Characterization data of 1,2-diaroylcarbohydrazides **3a- e**

Compd*	Ar	m.p. °C	Yield (%)	Mol. formula
3a	Phenyl	238-39	39.54	$C_{14}H_{12}N_2O_2$
3b	3-Tolyl	213	65.07	$C_{16}H_{16}N_2O_2$
3c	4-Tolyl	241-43	54.73	$C_{16}H_{16}N_2O_2$
3d	4-Chlorophenyl	288	64.84	$C_{14}H_{16}N_2O_2Cl_2$
3e	2-Furyl	223-24	46.12	$C_{10}H_8N_2O_4$

* All the compounds gave satisfactory elemental analyses

was decomposed in an ice-cold water containing conc. HCl (5mL) The solid obtained was filtered and washed with saturated sodium bicarbonate solution to remove acidic components. The compound was then purified by SiO_2 column chromatography using $CHCl_3$-EtOAc (80:20) as eluant. 1,5-Dibenzoylhydrazine **3a**, Ar=Ph was obtained in 39.57% yield.

A similar procedure was employed for the substrates **Ib-e** to get 1,2-diaroylhydrazines **3b-e**. The characterization data of **3a-e** are given in Table II.

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